

APPLICATION FOR LETTERS PATENT OF THE
UNITED STATES OF AMERICA

For the invention entitled:

CALCIUM HYPOCHLORITE OF REDUCED REACTIVITY

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1 CALCIUM HYPOCHLORITE OF REDUCED REACTIVITY

2

3 FIELD OF THE INVENTION

4 This invention relates to calcium hypochlorite blends;
5 particularly to blends of solid calcium hypochlorite in
6 combination with an alkali salt form(s) of anti-scaling
7 polymers, wherein the polymer(s) are present in an alkali
8 salt form effective at reducing the hygroscopic
9 characteristics of the solid polymer(s), and subsequent
10 calcium hypochlorite blend. This invention also relates to a
11 means of reducing the reactivity of solid calcium
12 hypochlorite with the said polymer(s) by applying a coating
13 of the polymer(s) to the solid calcium hypochlorite.

14

15 BACKGROUND OF THE INVENTION

16 U.S. Patents 5,112,521 and 5,004,549 disclose the
17 blending of Phosphono-Butane-Tricarboxylic acid (PBTC) with
18 calcium hypochlorite to produce a solid calcium hypochlorite
19 blend that inhibits scale formation associated with the
20 reconstitution and dispensing of the calcium hypochlorite
21 solution.

22 U.S. Patent 6,146,538, the contents of which are herein
23 incorporated by reference, discloses the use of Polymaleic
24 acid (PMA) and/or Polyepoxysuccinic acid (PESA) in an alkali

1 salt form that is blended with calcium hypochlorite to
2 reduce or eliminate scale formation associated with the
3 reconstitution and dispensing of the calcium hypochlorite
4 solution.

5 It is known that increased moisture, especially
6 localized moisture, increases the rate of decomposition of
7 calcium hypochlorite. During decomposition, oxygen is
8 released, with chlorides and chlorates typically being the
9 resulting byproducts. In the presence of sufficient
10 moisture, exothermic reactions result, oxygen release
11 increases, and a potential fire hazard is produced when fuel
12 sources are available, e.g. cloth, hydrocarbons and the
13 like.

14 PBTC disclosed in U.S. Patents 5,112,521 and 5,004,549,
15 when combined with calcium hypochlorite as an anti-scaling
16 agent, can nevertheless compromise manufacturing safety and
17 solid product stability, due to its inherent hygroscopic
18 characteristics.

19 It has now been discovered that the alkali salt forms
20 of PMA, PESA, and similar polymeric salts which are commonly
21 employed as deposit control agents, can significantly
22 reducing the hygroscopic characteristics of calcium
23 hypochlorite when combined therewith, in addition to
24 providing enhanced anti-scaling properties. It has been

1 further discovered that a coating of these polymers or
2 blends thereof significantly reduces the reactivity of the
3 solid calcium hypochlorite blend.

4 Thus, a step forward in the art is realized via
5 provision of a solid calcium hypochlorite combination which
6 simultaneously exhibits anti-scaling properties and reduced
7 hygroscopic and reactivity characteristics. Such a
8 composition yields improvements in both manufacturing safety
9 and product stability by reducing moisture adsorption and
10 subsequent decomposition of the calcium hypochlorite, as
11 well as improved safety by reducing the reactivity of the
12 solid calcium hypochlorite.

13

14 DESCRIPTION OF THE PRIOR ART

15 U.S. Pat. No. 4,146,676 describes calcium hypochlorite
16 particles coated with about 4 to 45 percent by weight of a
17 low melting inorganic salt, e.g. aluminum sulfate hydrates,
18 to reduce dusting during handling and to increase stability
19 of calcium hypochlorite contacted with lighted cigarettes or
20 reactive organic materials such as glycerine.

21 U.S. Pat. No. 4,965,016 describes a granular calcium
22 hypochlorite composition comprising a particle of calcium
23 hypochlorite, the surface of which has been covered with a
24 double decomposition product of calcium hypochlorite and an

1 alkali metal hydroxide. It was shown the granular strength
2 and stability was enhanced.

3 None of the prior art describes addition of an alkali
4 salt of an organic polymeric anti-scaling agent to provide
5 improved deposit control, while reducing the stability and
6 reactivity of the solid calcium hypochlorite.

7

8 SUMMARY OF THE INVENTION

9 The instant invention is directed toward a solid
10 calcium hypochlorite product formulation and a method for
11 its production, which product exhibits improved
12 environmental stability and shelf-life while simultaneously
13 inhibiting scale in dispensing equipment, as well as in and
14 on feed equipment used for delivering a calcium hypochlorite
15 solution to a water stream which is to be treated.

16 A solid calcium hypochlorite composition with improved
17 hygroscopic and reactivity characteristics is formulated
18 comprising hydrated calcium hypochlorite and an alkali salt
19 of Polymaleic acid, Polyepoxysuccinic acid or mixtures
20 thereof, having between 0.01 and 10% by weight of said
21 alkali salts, an available chlorine concentration of at
22 least 30% and water in the range of about 2% to about 20% by
23 weight.

24 In a particularly preferred embodiment, the composition

1 is a solid having greater than about 50% active Calcium
2 Hypochlorite which exhibits anti-scaling characteristics and
3 reduced hygroscopicity and reactivity.

4 The solid calcium hypochlorite may be coated and/or
5 encapsulated with at least one polymeric alkali salt
6 selected from within the group including polymaleate,
7 polyacrylate, polyacrylamide, polycarboxylate,
8 polymethacrylate, Phosphinopolycarboxylate, Carboxylate-
9 Sulfonate copolymer, Maleic Anhydride copolymer,
10 Polyepoxysuccinate, maleate-sulfonate copolymer, maleate-
11 phosphonate copolymer, carboxylate-phosphonate copolymer,
12 and/or mixtures thereof.

13 The alkali salt may be selected from at least one of
14 the group including the sodium, potassium, lithium, calcium,
15 or magnesium salts and mixtures thereof. Additionally, the
16 polymeric alkali salt may be in a liquid, slurry, or solid
17 form.

18 At some point in the manufacturing process the calcium
19 hypochlorite may be formulated/treated with a deposit
20 control agent including at least one alkali salt(s), e.g.
21 sodium, potassium, lithium, calcium, magnesium and/or
22 mixtures thereof, of polymaleic acid, polyexpoxysuccinic
23 acid, maleic anhydride copolymer, phosphinopolycarboxylic
24 acid, carboxylic-sulfonic acid copolymer, maleic-sulfonic

1 acid copolymer, maleic-phosphonic acid copolymer,
2 carboxylic-phosphonic acid copolymer, and/or mixtures
3 thereof. The weight percent of deposit control agent is
4 within the range of about 0.01% to about 10% of the final
5 weight of the formulated calcium hypochlorite product.

6 These polymers and copolymers will exhibit similar
7 hygroscopic characteristics in the desired salt forms while
8 providing deposit control capability. Furthermore, all are
9 hydrophilic and possess high thermal stability. Therefore
10 they will reduce reactivity of the solid calcium
11 hypochlorite product.

12 Accordingly, it is an objective of the instant
13 invention to provide a solid calcium hypochlorite product
14 and a method for its production, wherein the resultant
15 product exhibits reduced hygroscopic characteristics thereby
16 improving the manufacturing safety and shelf-life and anti-
17 scaling properties of the solid product.

18 It is a further objective of the instant invention to
19 provide a coated or encapsulated solid calcium hypochlorite
20 product having reduced reactivity and anti-scaling
21 properties.

22 Other objects and advantages of this invention will
23 become apparent from the following description taken in
24 conjunction with the accompanying drawings wherein are set

1 forth, by way of illustration and example, certain
2 embodiments of this invention. The drawings constitute a
3 part of this specification and include exemplary embodiments
4 of the present invention and illustrate various objects and
5 features thereof.

6

7 DETAILED DESCRIPTION OF THE INVENTION

8 As illustrated in Table 1, embodiments disclosed in
9 U.S. Patents 5,112,521 and 5,004,549 as well as an alkali
10 salt form of the Polymaleic acid disclosed in U.S. Patent
11 6,146,538 (all of which are herein incorporated by
12 reference) were tested for their hygroscopic properties by
13 exposing similar quantities of each to a controlled
14 atmospheric environment consisting of the following
15 approximate conditions:

16 72oF, and 50% humidity.

17 The samples were weighed and then exposed to the
18 controlled environment. The samples were weighed before and
19 after exposure. The increase in weight is associated with
20 the increased moisture.

21 The NaPBTC increased moisture through adsorbing
22 moisture from the surrounding environment.

23 It is understood that based upon the known reactivity
24 of calcium hypochlorite, which is a Class 3 oxidizer, and

1 its known increased decomposition with increased moisture,
2 that the addition of an anti-scaling agent that increases
3 hygroscopicity will lead to a potentially dangerous
4 situation. Thus, the instant invention provides a
5 combination of ingredients which simultaneously reduces the
6 hygroscopic characteristics
7 of the final solid product, thereby improving the
8 manufacturing safety and final product stability, while
9 ensuring chemical feed reliability through improved deposit
10 control.

TABLE 1

		Weight	Weight After	w/w % Change
		Before	2hr	2hr
13	Dry Polymaleate	0.99grams	1.01grams	2.02%
14	Polymer			
15	BAYHIBIT (PBTC)	1.09grams	1.27grams	16.51%
16			Weight	w/w % Change
17	Dry Polymaleate		After 24hr	24hr
			1.06grams	7.07%

18 Polymer
19 BAYHIBIT (PBTC) 1.93grams 77.06%
20 Adsorption of localized moisture creates the greatest
21 concern. While the % weight increase to a 1.5% blend would
22 appear to be minimal, localized moisture increase will
23 correlate to the data exemplified in Table 1, reducing shelf
24 life, chlorine activity, and potential increased risk of
25 combustion when fuel sources are contacted as outlined in

1 Table 2, below.

2 While not wishing to be bound to any particular
3 physical form, the combination of calcium hypochlorite and
4 polymer may be in the form of a homogeneous mixture, may
5 alternatively take the form of an outer layer or covering
6 which coats or encapsulates the cal-hypo for increased
7 stability and reduced reactivity, or a combination thereof.

8 Table 2 illustrates the reaction of 68% calcium
9 hypochlorite shock, sold under the brand name HTH SHOCK,
10 with and without a coating of a calcium polymaleate salt,
11 upon exposure to oil.

12 Each sample used approximately 7.5 grams of solid
13 calcium hypochlorite. The treated sample was mixed with 4.7
14 grams of polymer salt (slurry weight), followed by
15 convective drying. Each sample was placed in a dish where
16 1oz. of oil (brake fluid) was added as a fuel source.

17 The results clearly illustrate that coating the solid
18 calcium hypochlorite with a polymeric salt(s) of Polymaleic
19 acid or PESA as described in U.S. Patent 6,146,538
20 dramatically reduces the reactivity of calcium hypochlorite.
21 Even in the case of extended exposure to combustible
22 materials, the formulation described has the ability to
23 significantly reduce the rate of decomposition of the
24 calcium hypochlorite and prevent ignition when ignition

1 would otherwise occur without treatment. It is therefore
2 also reasonable to extrapolate from the data that further
3 improvement would be achieved by encapsulation of the solid
4 calcium hypochlorite.

5 TABLE 2

		Time to	Time to	
		Fuming	Combustion	Residue
7	HTH Shock	58	62	Charred, light
		seconds	seconds	weight, ash like

8	Treated HTH Shock	525	Not	No charred,
		seconds	Applicable	heavy, polymer residue

9 Additional tests were performed using various polymeric
10 salts with known anti-scaling abilities. These polymers all
11 possess thermal stability sufficient to prevent their
12 decomposition during exposure to exothermic reactions from
13 the decomposition of exposed calcium hypochlorite as well as
14 hot fuming fuels. The thermal stability ensures the polymer
15 coating prevents exposure of coated calcium hypochlorite
16 thereby preventing a self-sustaining decomposition or
17 runaway reaction.

18

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Salt samples of polyacrylate and polymaleate were produced for reactivity testing as illustrated in Table 3.

Table 3

4	Sample	Polymer Salt	Grams 68%	Grams Polymer
5		Form	Cal-Hypo	(solids)
6	1	Na/Ca Polyacrylate	45	Approx. 2
7	2	Ca Polyacrylate	45	Approx. 2
8	3	Na/Ca Polymaleate	45	Approx. 2

14 These polymer salt samples were applied in either the
15 form of a slurry or foam to 45 gram samples of >68% calcium
16 hypochlorite sold under the brand name HTH. Foam (table 4
17 sample 3b) was used to enhance the distribution of the
18 polymer. After drying, the treated samples were compared to
19 blank samples for reactivity. 10ml of brake oil fluid was
20 used as a fuel source, and the time from addition to fuming
21 and ignition was measured, along with their weights.

¹ Table 4 illustrates the results of the testing.

Table 4

3	Sample	Cal-hypo wt.	Total wt.	Fuming (sec)	Ignition (sec)	Final Weight	Appearance	Polymer
4		(gm)	(gm)			(gm)		applied
5	Untreated							
6	1	7.72	9.99	spilled	n/a	n/a	n/a	n/a
7	2	7.84	10.02	12	14	10.13	Charred Ash	n/a
8	3	7.81	9.99	13	15	9.74	Charred Ash	n/a
9	4	7.86	10.03	13	15	9.37	Charred Ash	n/a
10								
11								
12	Treated							
13		7.88	9.95	100	N/A	15.97 Cal-hypo residue	Slurry	
14		7.77	10.03	105	N/A	16.8 Cal-hypo residue	Slurry	
15		7.89	9.99	45	N/A	14.67 Cal-hypo residue	Slurry	
16		7.88	9.92	195	N/A	18.83 Cal-hypo residue	Foam	

The results of these test illustrate that treating the

18 >68% calcium hypochlorite with an alkali salt form of
19 hydrophilic polymer with thermal stability exceeding 300°F
20 significantly reduces the reactivity of the calcium
21 hypochlorite.

22 The reaction is self-limiting in that only exposed
23 (untreated) calcium hypochlorite is involved in the reaction
24 and once consumed in the reaction, residual fuel remains in
25 contact with the stabilized (treated) calcium hypochlorite.

These test results further illustrate that by limiting exposure of calcium hypochlorite to the fuel source, the rate of reaction is significantly reduced, and ignition is avoided all together.

30 Yet another result of these tests is that increased
31 coverage of the calcium hypochlorite yields further

1 reduction in reactivity of the treated calcium hypochlorite.
2 In this example, application of the polymer by use of an
3 expanded foam to increase its volume improved coverage and
4 distribution, correlating to improved performance at
5 reducing the samples reactivity.

6 As previously presented, improving the hygroscopic
7 characteristics of the calcium hypochlorite improves the
8 manufacturing safety and shelf-life of the solid product.
9 This is true regardless of whether the solid product is in a
10 granular, pellet, tablet or briquette form. By adding an
11 anti-scaling agent with improved hygroscopic
12 characteristics, the potential for compromising safety and
13 shelf-life is reduced.

14 By reducing the surface area of the calcium
15 hypochlorite by coating the solid material with a
16 hydrophilic polymeric salt with thermal stability exceeding
17 300oF, the reactivity of the calcium hypochlorite is
18 reduced, while allowing rapid dissolution of the calcium
19 hypochlorite when diluted with water, as in the case of a
20 calcium hypochlorite dispenser.

21 To further improve the hygroscopic characteristics of
22 the hydrophilic salt, divalent salts, or increased
23 percentages thereof, should be included in the final salt
24 form of the polymer.

1 It is to be understood that while a certain form of the
2 invention is illustrated, it is not to be limited to the
3 specific form or arrangement of parts herein described and
4 shown. It will be apparent to those skilled in the art that
5 various changes may be made without departing from the scope
6 of the invention and the invention is not to be considered
7 limited to what is shown and described in the specification.

8 One skilled in the art will readily appreciate that the
9 present invention is well adapted to carry out the objects
10 and obtain the ends and advantages mentioned, as well as
11 those inherent therein. The compounds, compositions, and any
12 biologically related compounds, methods, procedures and
13 techniques described herein are presently representative of
14 the preferred embodiments, are intended to be exemplary, and
15 are not intended as limitations on the scope. Changes
16 therein and other uses will occur to those skilled in the
17 art, which are encompassed within the spirit of the
18 invention and are defined by the scope of the appended
19 claims.

20 Although the invention has been described in connection
21 with specific preferred embodiments, it should be understood
22 that the invention as claimed should not be unduly limited
23 to such specific embodiments. Indeed, various modifications
24 of the described modes for carrying out the invention which

1 are obvious to those skilled in the art are intended to be
2 within the scope of the following claims.

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